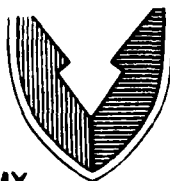


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US ARMY
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MTL TR 86-31

VO₂ THIN FILMS

July 1986

Y. HUI, R. BRUSASCO, R. KERSHAW, K. DWIGHT, and A. WOLD
Brown University, Providence, RI 02912

W. CROFT
Materials Characterization Division

INTERIM REPORT

Contract No. DAAG46-83-K-0015

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ABSTRACT

Amorphous films of vanadium dioxide have been prepared by the thermal decomposition of vanadium acetylacetonate in a CO/CO₂ atmosphere. Films have been deposited on glass and quartz.



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VO₂ THIN FILMS

Vanadium (IV) oxide shows a transition at 67°C from a semiconductor to a metallic phase. Whereas there have been many studies dealing with the electrical and magnetic properties of these phases, the study of the optical properties has been hindered (1, 2) by the lack of single crystals of sufficient size and mechanical strength for the preparation of thin wafers for optical transmission (3).

Merenda and Sol (4) have succeeded in growing high quality (1 cm² area, 1 to 30 μm thickness) of pure VO₂ by chemical vapor deposition on TiO₂ substrates. The chemical vapor deposition occurred by reacting a VOCl₃/H₂O/H₂ mixture at about 800°C using argon as a carrier gas. The preparation of pure VO₂ required care to make it homogeneously stoichiometric and also to obtain steep concentration profiles at the TiO₂/VO₂ interface. The single crystalline layers were grown at a rate of 10 μ/hr and the impurity content was much lower than most bulk grown crystals. Films were grown which were stoichiometric as well as layers rich or deficient in oxygen.

In order to prepare thin VO_2 films on III-V semiconductors, it will be necessary to find a procedure which has a maximum deposition temperature of 350°C . The III-V semiconductor begins to decompose when heated above this temperature.

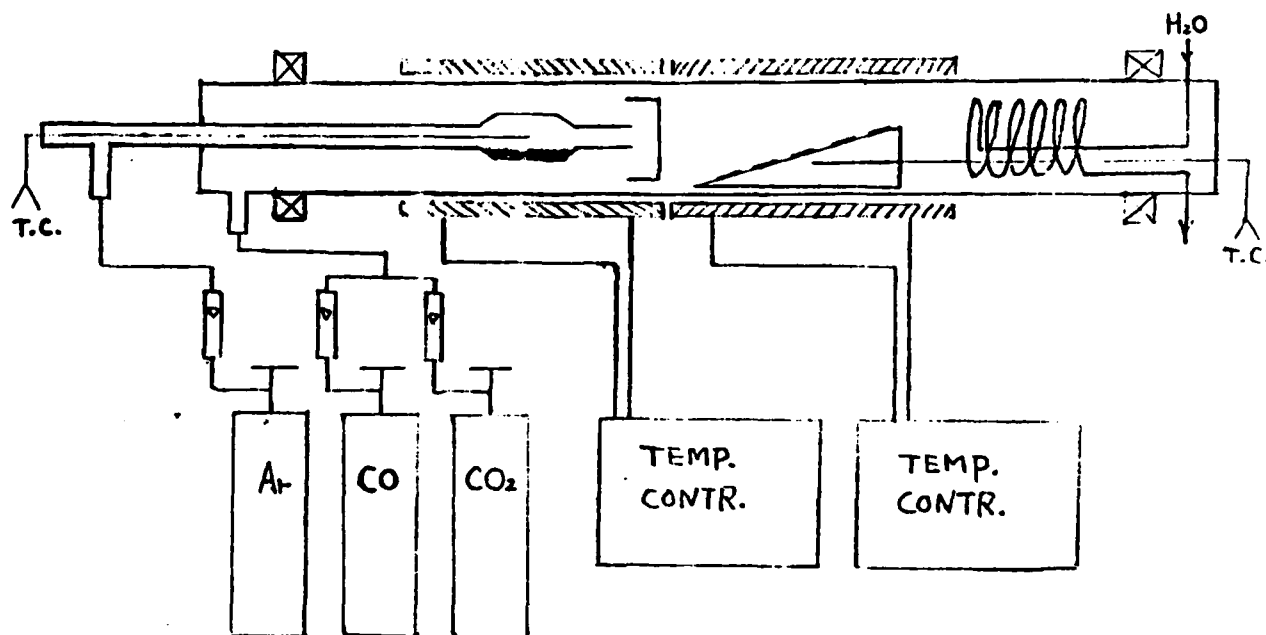
It was found in our laboratory that vanadium acetylacetonate, $\text{V}(\text{AcAc})_3$, has a high volatility at 190°C and can be used as the transporting compound. The stabilization of the +4 valence state could be achieved by carrying out the decomposition of $\text{V}(\text{AcAc})_3$ in a CO/CO_2 atmosphere. The partial pressure of the oxygen under such conditions can be defined by the following relation

$$\log p_{\text{O}_2} = A - \left(\frac{29560}{T}\right) + 2 + \log \left| \frac{R}{1-R} \right|$$

$$R = \frac{\text{CO}_2}{\text{CO} + \text{CO}_2}$$

A = constant

T = Temperature K



A two zone reactor was designed as shown in Figure 1. Argon gas is allowed to flow over the source material and a mixture of CO/CO₂ is introduced into the reactor in order to decompose the complex. The substrates are placed at an angle to the exit baffle which homogeneously distributes the carrier gas and reactants.

Preliminary Results and Discussion

The melting point of $V(\text{AcAc})_3$ is 185-190°C and its volatility as a function of temperature was measured. It was found that at 190°C, an appreciable volatility of the complex was obtained. Of the various substrates which could be selected, SiO_2 and glass were chosen because of the suitability as supports for optical measurements. The substrates were treated in the following manner:

The substrates were soaked in aqua regia for five hours. They were then washed with distilled water, ethanol, and finally acetone. The substrates were then placed in an ultrasonic cleaner and washed 3 times with water, ethanol and acetone. They were then given a final treatment in boiling distilled water and dried just before being used in the reactor.

In our preliminary experiments the conditions for film growth were adjusted as follows:

Source material temperature	190°C
Ar carrier gas flow	60 cc/min
$\text{CO} + \text{CO}_2$	120 cc/min
$\text{CO}_2/\text{CO} + \text{CO}_2$	• 85
Substrate temperature	450°C

Vanadium oxide films were obtained on SiO_2 and glass. The films were not of uniform thickness and were black or dark grey in color. Upon cooling of the films to room temperature, it was noted that adhesion to the glass was poor. Adhesion seemed to improve upon annealing the films in sealed evacuated tubes for at least one day at 450°C. X-ray diffraction peaks of the films prepared on

glass showed them to be amorphous. Further studies are in progress.

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Interim Report, Aug. 1985 to July 1986

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